PATENT ABSTRACTS OF JAPAN

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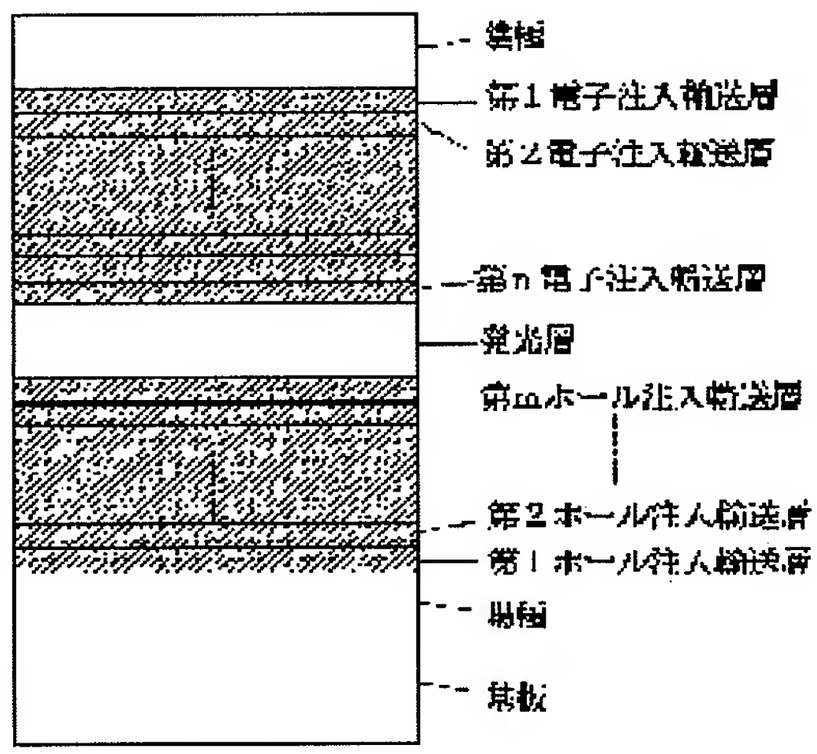
(54) ORGANIC THIN FILM ELECTROLUMINESCENT ELEMENT HAVING PLURAL CARRIER INJECTION LAYER

(57)Abstract:
PURPOSE: To lower an element driving voltage and to enhance the durability of an element by inserting a plurality of carrier injection layers into the boundary face between an anode and a luminous layer and into the boundary face between a cathode and the luminous layer.
CONSTITUTION: An organic thin film electroluminescent element comprises an anode, a hole injection transport layer, a luminous layer, an electron injection transport layer and a cathode, and either or both of the hole injection transport layer and the electron injection transport layer are divided into plural layers. The ionization potential value of the hole injection transport layer is in a predetermined relationship to the work function value of the anode, and the value of electron affinity of the electron injection layer is in a predetermined relationship to the work function of the cathode. A hole injection barrier from the anode to the luminous layer and an electron injection barrier from the cathode to the luminous layer can be reduced significantly and thereby a driving voltage is lowered and the crystallization of the organic layers due to Joule heat is restrained so that durability of the element can be enhanced.



* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1]In an organic thin film EL element which comprises the anode / a hole pouring transporting bed / a luminous layer / an electron injection transporting bed / the negative pole, At least one side of a hole pouring transporting bed and an electron injection transporting bed consists of a layer more than two-layer, value Eae1 of each electron affinity of an electron injection transporting bed of two or more layers, Eae2, and ... Eaen (n here that an electron injection transporting bed comprises a n layer) [mean and] 1, 2, and ... n means turn from the negative pole side. A value (Ipc) of a work function of the negative pole, and a relation of following formula (I), [satisfy and] And value Iph1 of each ionization potential of a hole pouring transporting bed of two or more layers, Iph2 ... Iphm (m here that a hole pouring transporting bed comprises an m layer) [mean and] 1, 2, and ... m means turn from the anode side. An organic thin film EL element satisfying a value (Ipa) of a work function of the anode, and a relation of following formula (II).
Ipc>=Eae1>=Eae2>= ... >=Eaen (I)
Ipa<=Iph1<=Iph2<= ... <=Iphm (II)
[Claim 2]In an organic thin film EL element which comprises the anode / a hole pouring transporting bed / a luminous layer / the negative pole, a hole pouring transporting bed consists of a layer more than two-layer at least -- value Eae1 of each electron affinity of an electron injection transporting bed of two or more layers, Eae2, and ... Eaen (n here that an electron injection transporting bed comprises a n layer) [mean and] 1, 2, and ... n means turn from the negative pole side. A value (Ipc) of a work function of the negative pole, and a relation of following formula (I), [satisfy and] And value Iph1 of each ionization potential of a hole pouring transporting bed of two or more layers, Iph2 ... Iphm (m here that a hole pouring transporting bed comprises an m layer) [mean and] 1, 2, and ... m means turn from the anode side. An organic thin film EL element satisfying a value (Ipa) of a work function of the anode, and a relation of following formula (II).
Ipc>=Eae1>=Eae2>= ... >=Eaen (I)
Ipa<=Iph1<=Iph2<= ... <=Iphm (II)
[Claim 3]value Eae1 of each electron affinity of an electron injection transporting bed of two or more layers, Eae2, and ... Eaen (n here that an electron injection transporting bed comprises a n layer) [mean and] 1, 2, and ... n means turn from the negative pole side. A value (Ipc) of a work function of the negative pole, and a relation of following formula (I), [satisfy and] And value Iph1 of each ionization potential of a hole pouring transporting bed of two or more layers, Iph2 ... Iphm (m here that a hole pouring transporting bed comprises an m layer) [mean and] 1, 2, and ... m means turn from the anode side. An organic thin film EL element satisfying a value (Ipa) of a work function of the anode, and a relation of following formula (II).
Ipc>=Eae1>=Eae2>= ... >=Eaen (I)
Ipa<=Iph1<=Iph2<= ... <=Iphm (II)
[Claim 4]The organic thin film EL element according to claim 1, 2, or 3, wherein thickness of each class of one layer or a hole pouring transporting bed formed from two or more layers, and/or an electron injection transporting bed is 1000A or less.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention has a luminous layer which consists of a luminescent organic compound, and relates to the organic thin film EL element which can transform electrical energy into light energy directly by the recombination of the electrification carrier (an electron and a hole) poured into the luminous layer by the applied electric field.
[0002]
[Description of the Prior Art]In recent years, the needs for a flat-surface display device with few space occupation areas are growing with low power consumption rather than CRT with diversification and space-saving-izing of information machines and equipment. Although there are a liquid crystal, a plasma display, etc. as such a flat-surface display device, the expectation for the organic thin film EL element in which a DC voltage drive is possible has been growing vividly [a display] with the self-luminescence type especially recently.
[0003]Two-layer structure proposed by C.W.Tang and others of Kodak as element structure of an organic thin film EL element until now (between the anode and the negative pole) The structure (SH-A structure) (JP,59-194393,A, Appl.Phys.Lett.51,913 (1987)) where the hole transporting bed and the electron-transport-property luminous layer were formed, The structure (SH-B) (USP No.5, 085947, JP,2-25092,A, Appl.Phys.Lett.55-1489 (1989)) where the hole transportability luminous layer and the electron transport layer were formed between the anode and the negative pole which were proposed by the group of Kyushu University, Or a three-tiered structure (there is structure (DH structure) (Appl.Phys.Lett.57,531 (1990)) where the hole transporting bed, the luminous layer, and the electron transport layer were formed between the anode and the negative pole.) By using three kinds of such element structures, the high-intensity EL luminescence over red is obtained from the blue more than 1000 cd/m^2 in first stage.
[0004]C.W. Although it is reported that the endurance excellent in using a triphenyl diamine derivative for a hole transporting bed, and using tris(eight quinolinol) aluminum for a luminous layer is shown, the element of the SH-A structure proposed by Tang and others, Since it does not have an electron transport layer which has hole block ability in the case of this element structure, when a prolonged continuation drive is performed, delicate pouring balance collapses, and a luminescence site (carrier recombination site) spreads, therefore the problem that degradation arises intrinsically is held. Since the hole transporting bed which has electronic block ability does not exist, crystallization of an electron transport layer occurs by continuation drive especially as expansion of the same luminescence site as the case of SH-A structure, and a still more serious problem, and the case of SH-B structure also has the problem that degradation of an element arises. In DH structure, since the luminescence site is restricted by the hole transporting bed and the electron transport layer, should not generate, but should pass through expansion of a luminescence site intrinsically, and should not produce degradation at the time, but. At present, the big problem is held in the endurance of an element by various factors (formation of space charge, etc.) which crystallization of an electron transport layer causes.
[0005]As one trial of durability enhancement, C.W.Tang and others has reported that improvement in endurance is possible by reducing the hole pouring barrier from (JP,63-

295695,A) and the anode to a hole transporting bed and a luminous layer by the three-tiered structure which inserted the hole pouring layer in SH-A structure. Thus, for the durability enhancement of an element, it has turned out that the detailed materials design to a hole and an electron injection process is required. Although the examination to a hole pouring process has been started a little as mentioned above, the electronic design manual of the component is not clear yet enough. On the other hand, about the electron injection process, an examination detailed until now is not made at all.

[0006]

[Problem(s) to be Solved by the Invention]By inserting a two or more layers carrier injection layer in both the interface of the anode and a luminous layer, and both [either or] of the negative pole and a luminous layer, this invention reduces element driver voltage, and [especially] it is providing the organic thin film EL element excellent in endurance.

[0007]

[Means for Solving the Problem]In an organic thin film EL element which comprises the anode / a hole pouring transporting bed / a luminous layer / an electron injection transporting bed / the negative pole according to this invention, At least one side of a hole pouring transporting bed and an electron injection transporting bed consists of a layer more than two-layer, value Eae1 of each electron affinity of an electron injection transporting bed of two or more layers, Eae2, and ... Eaen (n here that an electron injection transporting bed comprises a n layer) [mean and] 1, 2, and ... n means turn from the negative pole side. A value (Ipc) of a work function of the negative pole, and a relation of following formula (I), [satisfy and] And value Iph1 of each ionization potential of a hole pouring transporting bed of two or more layers, Iph2 ... Iphm (m here that a hole pouring transporting bed comprises an m layer) [mean and] 1, 2, and ... m means turn from the anode side. Ipc>=Eae1>=Eae2>= ... an organic thin film EL element satisfying a value (Ipa) of a work function of the anode and a relation of following formula (II) is provided -- >=Eaen (I)

Ipa<=Iph1<=Iph2<= ... <=Iphm (II)

In an organic thin film EL element which comprises the anode / a hole pouring transporting bed / a luminous layer / the negative pole, a hole pouring transporting bed consists of a layer more than two-layer at least -- value Eae1 of each electron affinity of an electron injection transporting bed of two or more layers, Eae2, and ... Eaen (n here that an electron injection transporting bed comprises a n layer) [mean and] 1, 2, and ... n means turn from the negative pole side. A value (Ipc) of a work function of the negative pole, and a relation of following formula (I), [satisfy and] And value Iph1 of each ionization potential of a hole pouring transporting bed of two or more layers, Iph2 ... Iphm (m here that a hole pouring transporting bed comprises an m layer) [mean and] 1, 2, and ... m means turn from the anode side. Ipc>=Eae1>=Eae2>= ... an organic thin film EL element satisfying a value (Ipa) of a work function of the anode and a relation of following formula (II) is provided -- >=Eaen (I)

Ipa<=Iph1<=Iph2<= ... <=Iphm (II)

value Eae1 of each electron affinity of an electron injection transporting bed of two or more layers, Eae2, and ... Eaen (n here that an electron injection transporting bed comprises a n layer) [mean and] 1, 2, and ... n means turn from the negative pole side. A value (Ipc) of a work function of the negative pole, and a relation of following formula (I), [satisfy and] And value Iph1 of each ionization potential of a hole pouring transporting bed of two or more layers, Iph2 ... Iphm (m here that a hole pouring transporting bed comprises an m layer) [mean and] 1, 2, and ... m means turn from the anode side. Ipc>=Eae1>=Eae2>= ... an organic thin film EL element satisfying a value (Ipa) of a work function of the anode and a relation which is following formula (II) is provided -- >=Eaen (I)

Ipa<=Iph1<=Iph2<= ... <=Iphm (II)

An organic thin film EL element of the upper part, wherein thickness of each class of one layer or a hole pouring transporting bed formed from two or more layers, and/or an electron injection transporting bed is 1000A or less is provided.

[0008]As a result of repeating examination wholeheartedly about a hole pouring process and an electron injection process, this invention persons in any of an interface of the anode and a

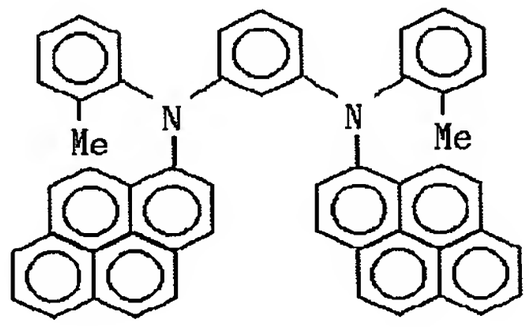
luminous layer, and an interface of the negative pole and a luminous layer or by inserting a two or more layers carrier injection layer in both, It finds out that an organic thin film EL element excellent in endurance is attained, and came to complete this invention. In the case of the conventional EL element, a hole pouring barrier from the anode to a luminous layer and an electron injection barrier from the negative pole to a luminous layer were large, crystallization of an organic layer by Joule heat was caused, and there was a problem in endurance. Especially about an electron injection process, by some which inserted one layer of the conventional electron transport layers, an electron injection barrier is large and there was a problem. Two or more carrier injection [this invention] transporting bed, Namely, a carrier injection barrier can be remarkably fallen by inserting two or more hole pouring transporting bed (layer which carries out pouring transportation of the hole from the anode to a luminous layer) and/or two or more electron injection transporting beds (layer which carries out pouring transportation of the electron from the negative pole to a luminous layer), It becomes possible to aim at a fall of driver voltage, and improvement in endurance. For durability enhancement, it is more desirable to satisfy the electronic state by which each carrier injection transporting bed, i.e., an electron injection transporting bed of two or more layers, and a hole pouring transporting bed of two or more layers are shown by said formula (I) and formula (II).

[0009]It describes below about a desirable material which constitutes a multilayer EL element. A substance which has strong fluorescence in a solid as a luminous layer material, and forms a precise film in a thin film of 500A or less is preferred. All conventionally publicly known materials used for a luminous layer of an organic EL device so far are applicable to an EL element of this invention. a metal chelate-ized oxy NOIDO compound (8-hydroxyquinoline metal complex) (JP,59-194393,A.) A butadiene derivative like JP,63-295695,A, 1,4-diphenylbutadiene, and tetraphenylbutadiene, A coumarin derivative, a benzoxazole derivative, an oxadiazole derivative, An oxazole derivative, a thiadiazole derivative, a styryl amine derivative, A screw styryl benzene derivative (JP,2-247277,A), a tris styryl benzene derivative (JP,3-296595,A), screw styryl anthracene derivative (JP,3-163186,A) and peri non -- a derivative, an amino pyrene derivative (a screw type metal chelate-ized oxy NOIDO compound of USP5,151,629 statement and USP5,150,006 statement is an outstanding luminous layer material.), etc. An example of a useful luminous layer material is shown in Table 1 below.

[0010]

[Table 1-(1)]

EML 1



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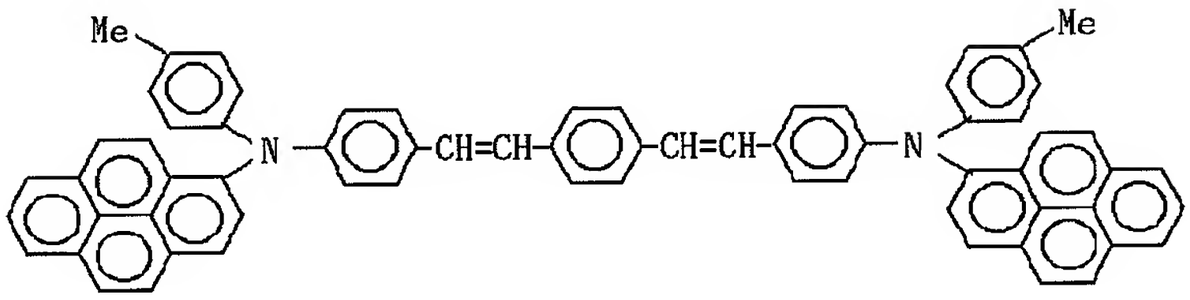

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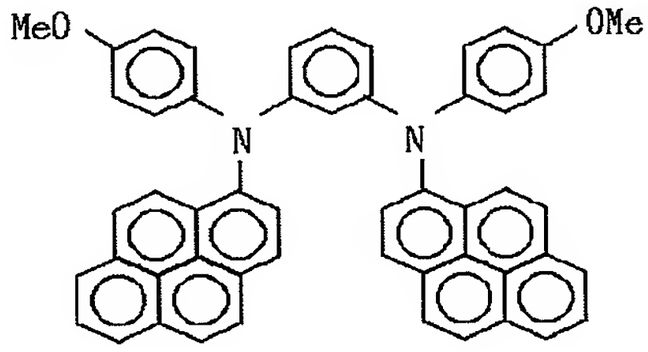

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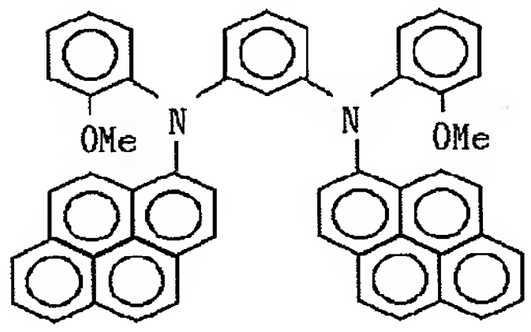

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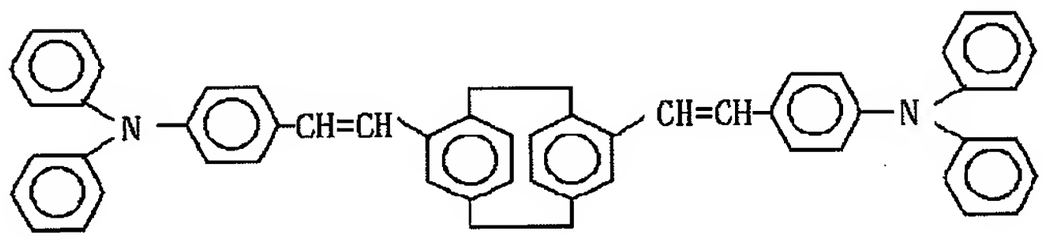

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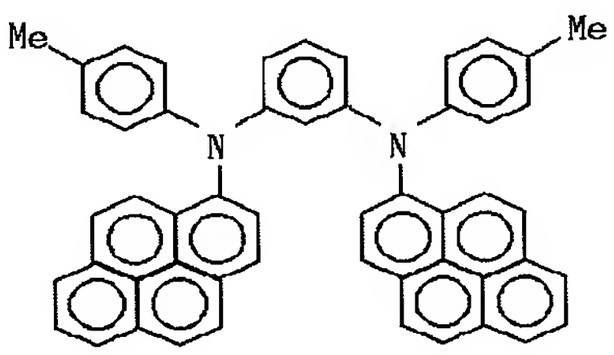

[0011]
[Table 1-(2)]

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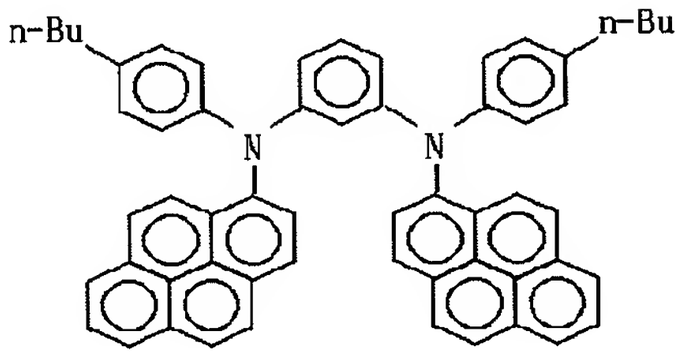

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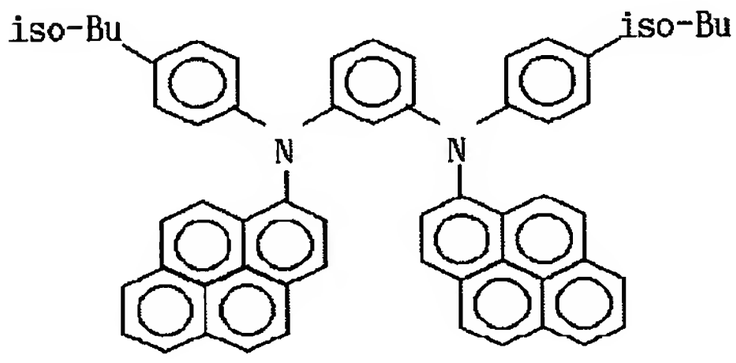

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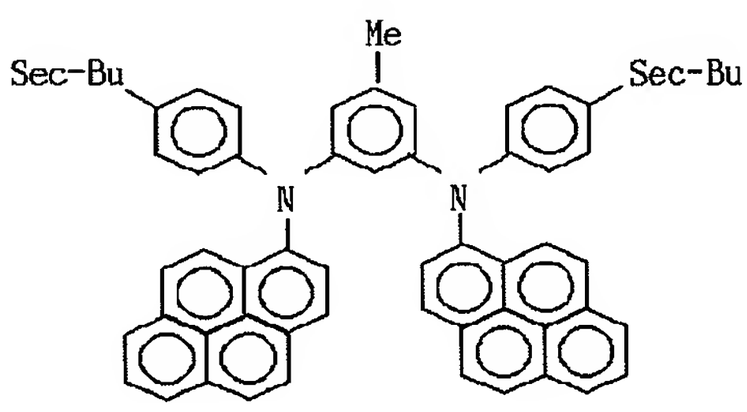

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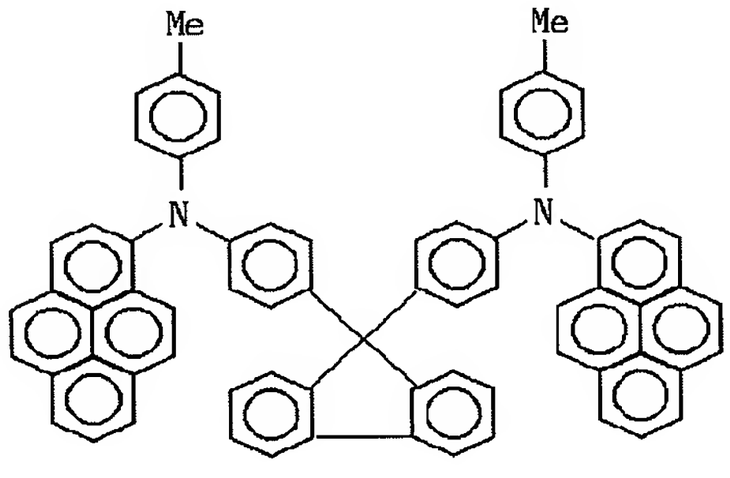

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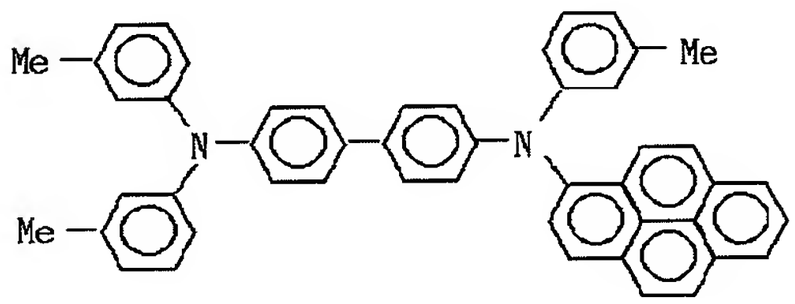
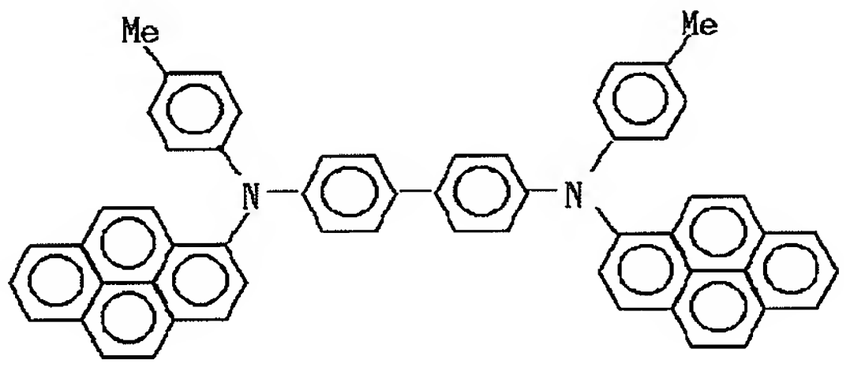
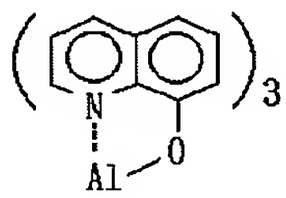
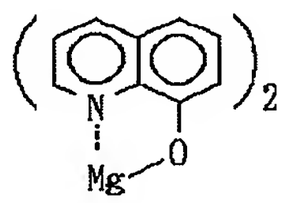
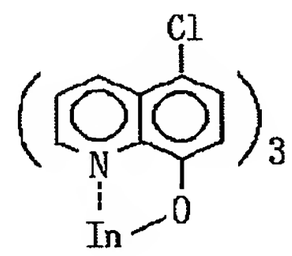


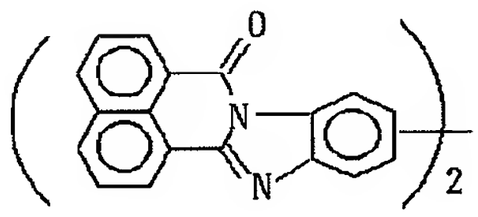
[0012]
[Table 1-(3)]

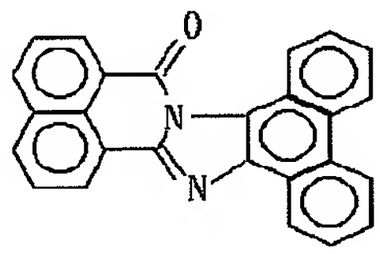
EML12 

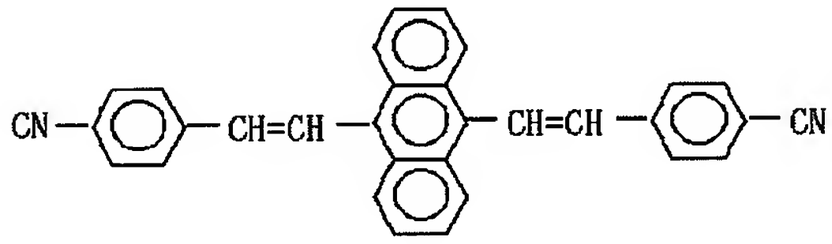
EML13 

EML14 

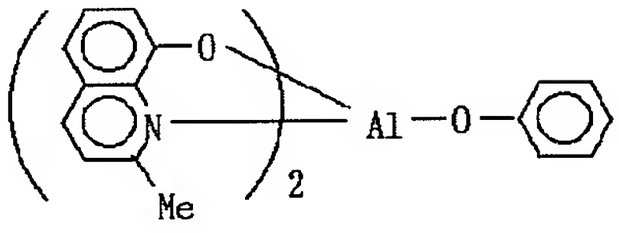
EML15 

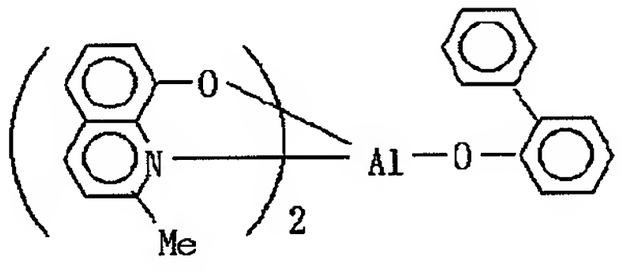
EML16 

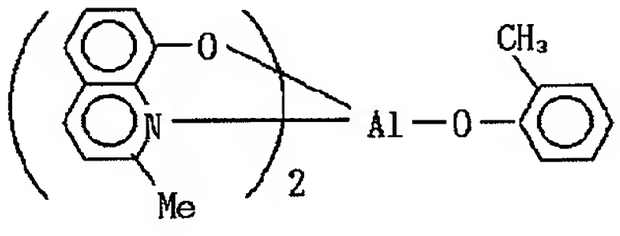
EML17 

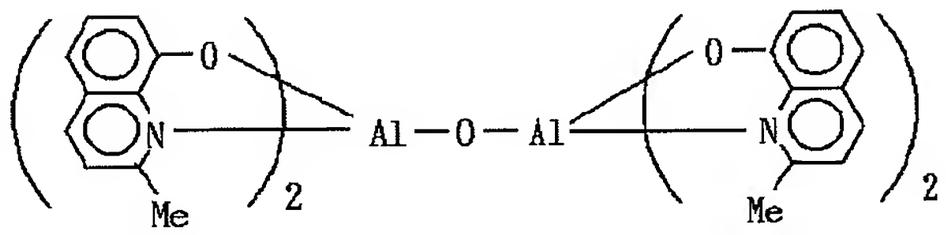
EML18 

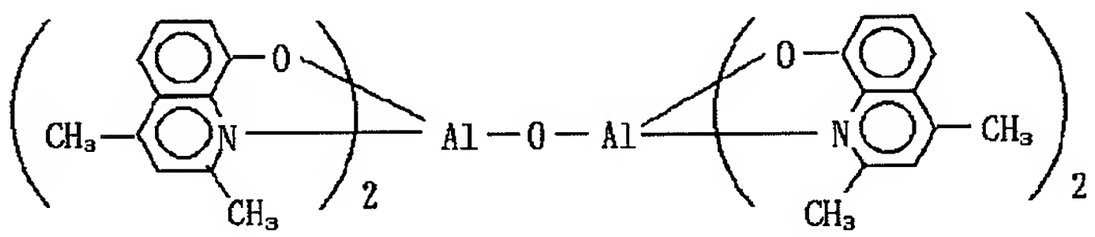
[0013]
[Table 1-(4)]

EML19 

EML20 

EML21 

EML22 

EML23 

[0014]As a hole pouring transporting bed material, although all publicly known materials can be conventionally used as a hole transporting bed material until now, at least two aromatic tertiary amine is included preferably -- desirable -- aromatic tertiary amine -- monoarylamine, diarylamine, and doria -- it is reel amine. A typical useful compound which carries out aromatic tertiary amine and is indicated by USP No.4,175,960, USP No.4,539,507, JP,63-264692,A, and JP,4-308688,A can be used. The Pori Phi Lynne derivative (phthalocyanines) currently indicated by USP No.4,720,432 is also a useful compound. An example of a useful hole pouring transporting bed material is shown in Table 2 below. When it constitutes a hole pouring transporting bed from two or more layers, laminating order which satisfies said formula (II) is preferred to durability enhancement.

[0015]

[Table 2-(1)]

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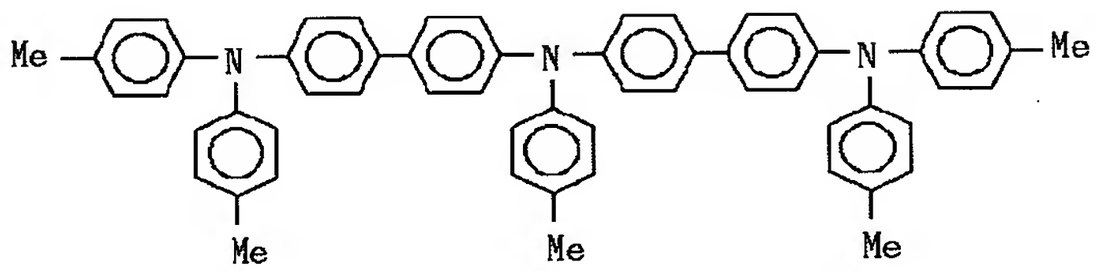

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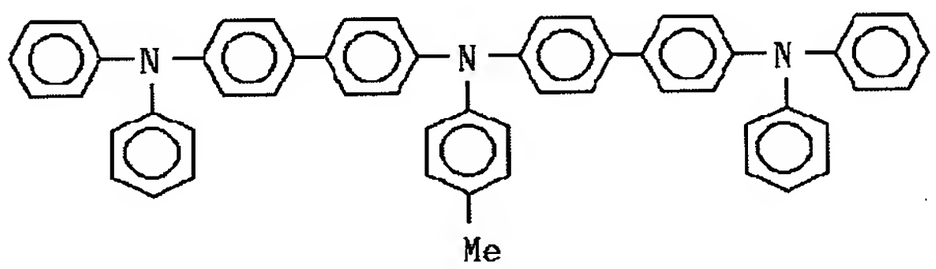

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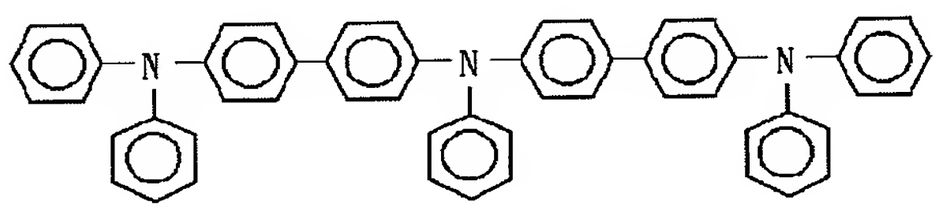

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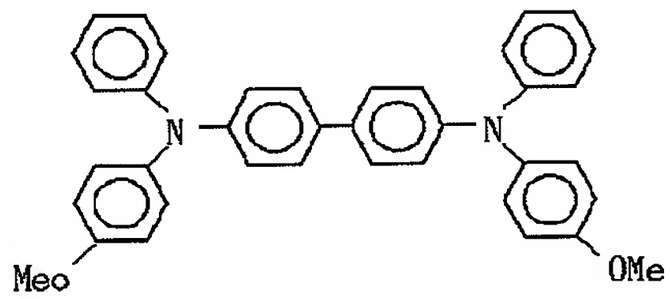

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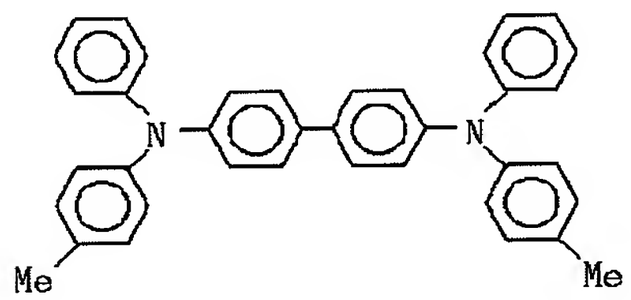

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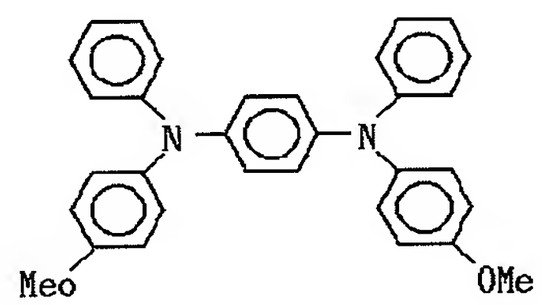
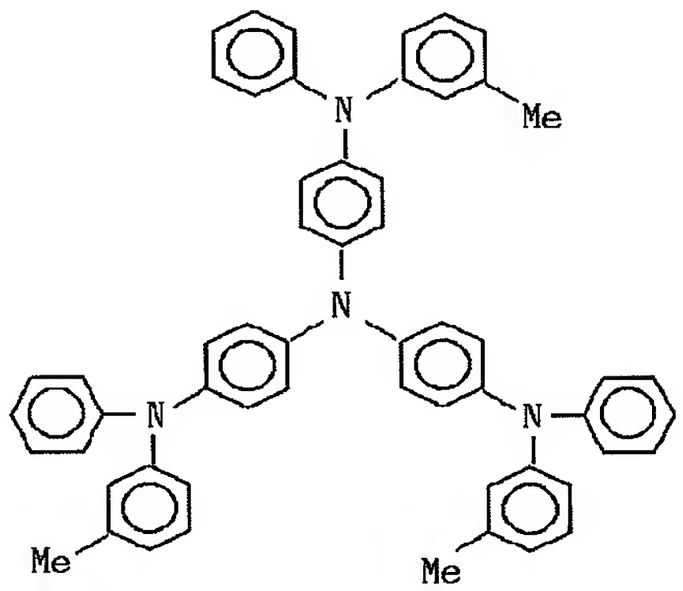
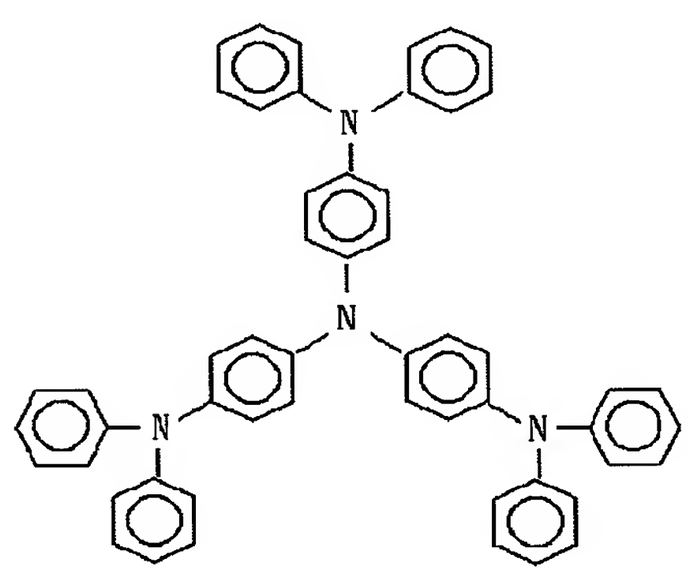


[0016]
[Table 2-(2)]

HTL7



HTL8

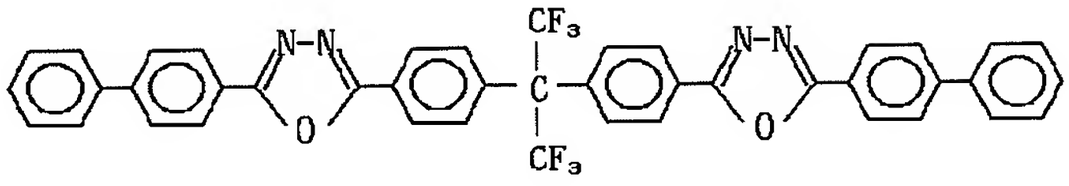


HTL9 iron-phthalocyanine HTL10 indium-chloride phthalocyanine HTL11 vanadyl-chloride phthalocyanine HTL12 magnesium phthalocyanine HTL13 Nickel phthalocyanine HTL14 zinc-phthalocyanine HTL15. Free metal naphthalocyanine HTL16 copper naphthalocyanine HTL17 iron naphthalocyanine HTL18 copper-phthalocyanine HTL19 free metal phthalocyanine HTL20 Titanylphthalocyanine[0017]As an electron injection transporting bed material, all the conventionally publicly known materials used as an electron transport layer material so far can be used. One desirable electron injection transported material is a compound containing at least one or more oxadiazole rings which are the manifestation units of electron transportation ability. In order to raise endurance, the compound containing two or more oxadiazole rings is preferred. The typical useful oxadiazole compound is indicated by Appl.Phys.Lett55-1489 (1989) and the Chemical Society of Japan 1540 (1991). The example of a useful oxadiazole compound is shown in Table 3 below.

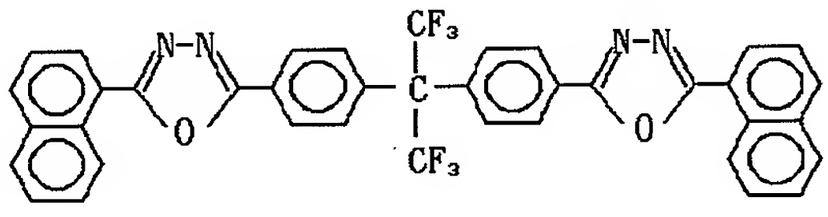
[0018]

[Table 3-(1)]

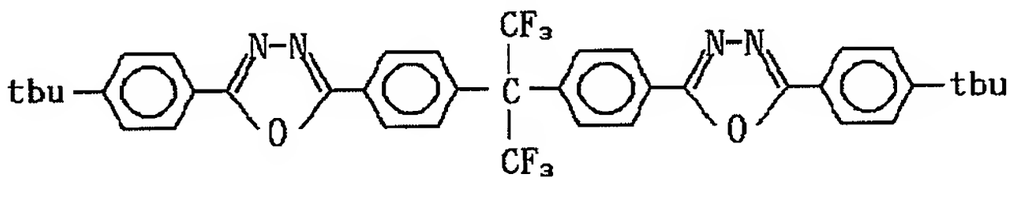
ETL1



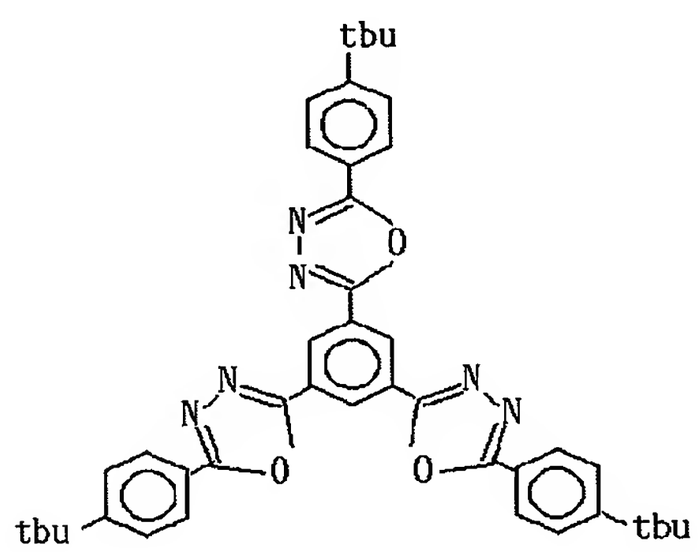
ETL2



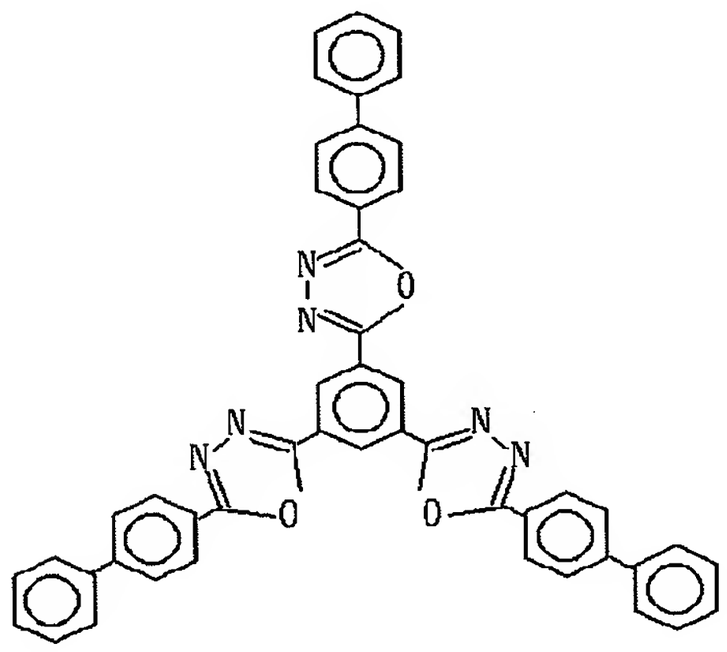
ETL3



ETL4

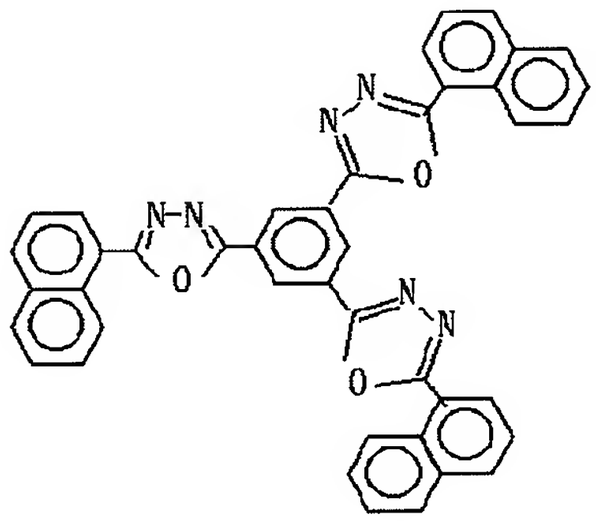


ETL5

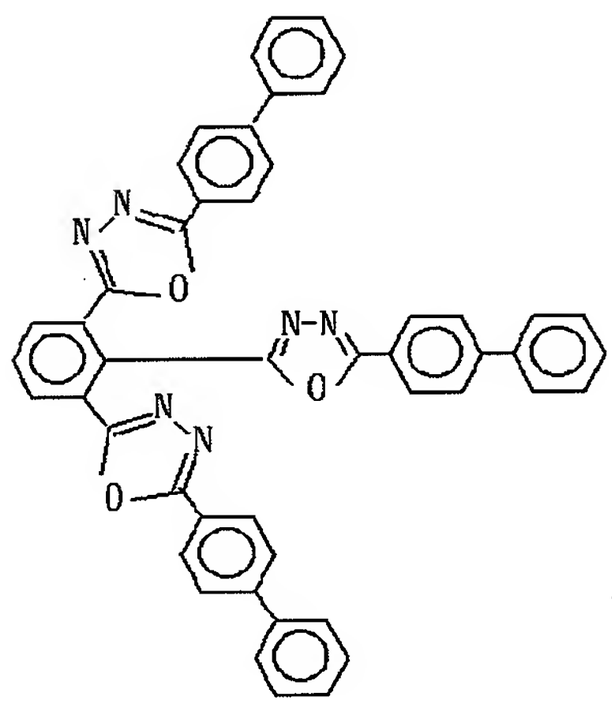


[0019]
[Table 3-(2)]

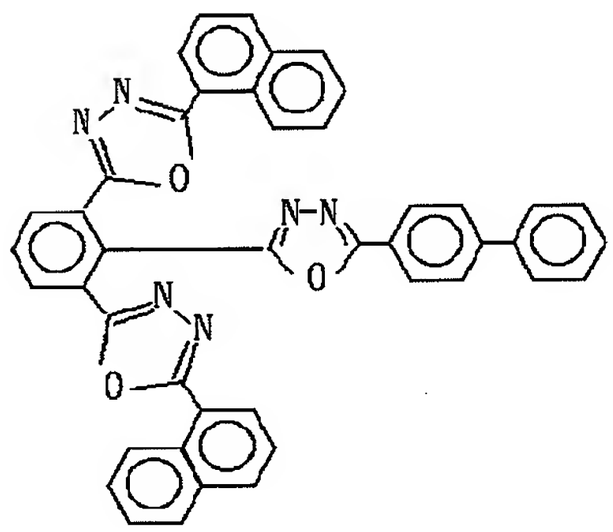
ETL6



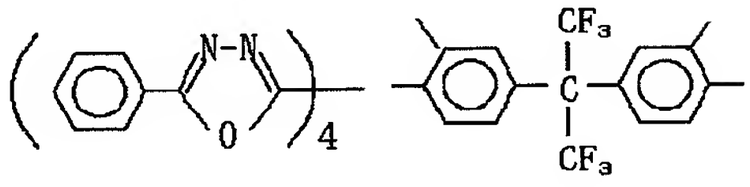
ETL7

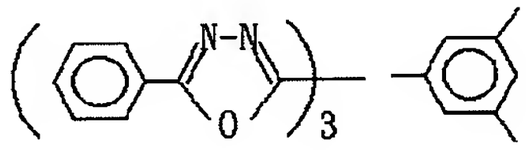


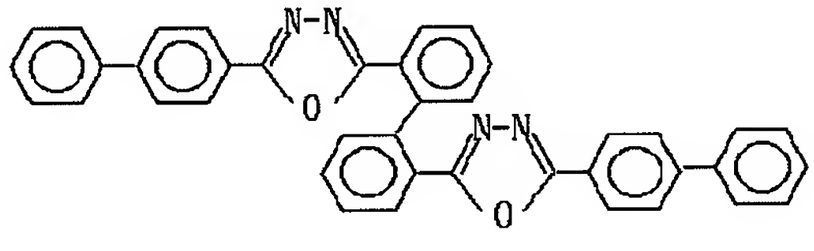
ETL8

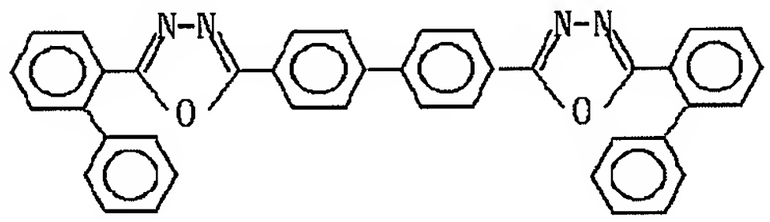


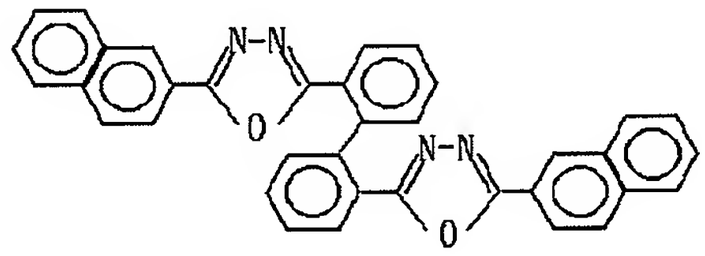
[0020]
[Table 3-(3)]

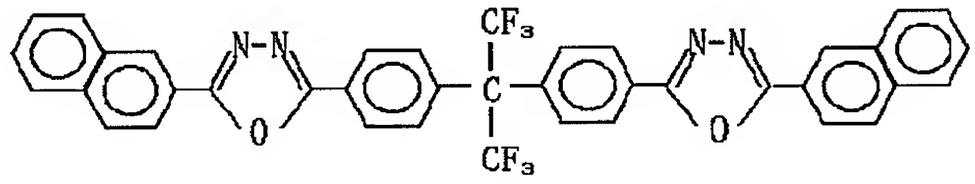
ETL9 

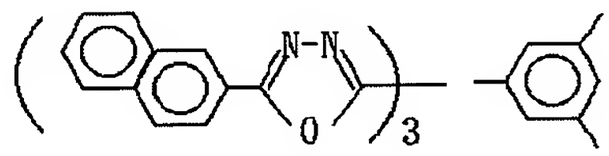
ETL10 

ETL11 

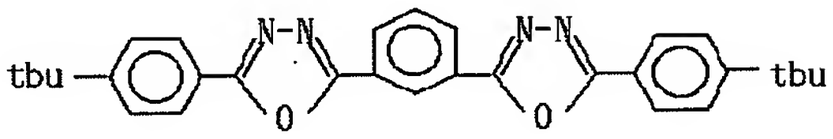
ETL12 

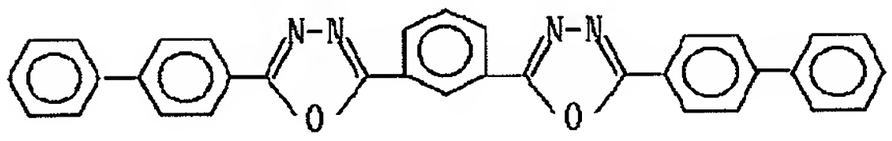
ETL13 

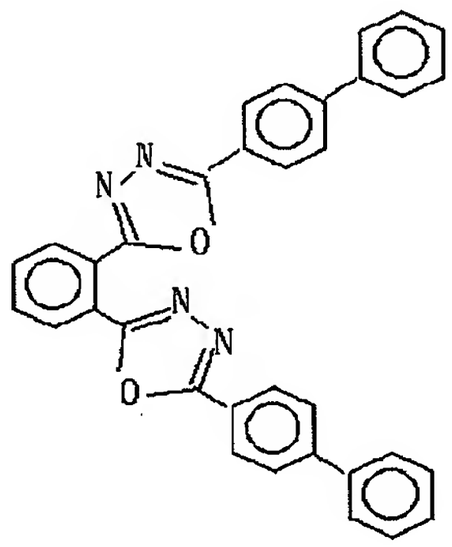
ETL14 

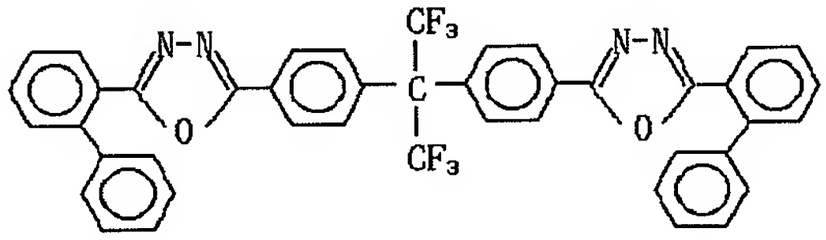
ETL15 

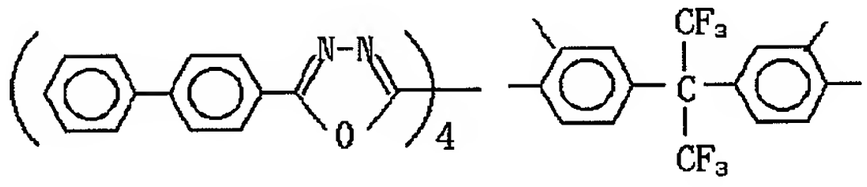
[0021]
[Table 3-(4)]

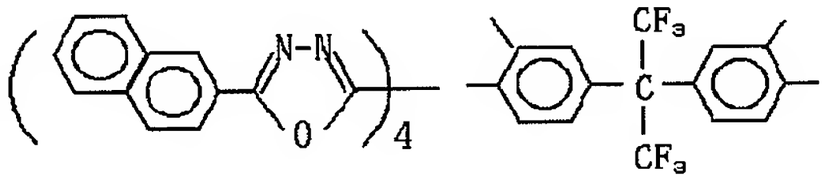
ETL16 

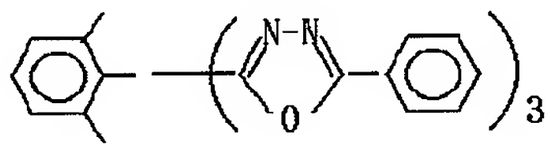
ETL17 

ETL18 

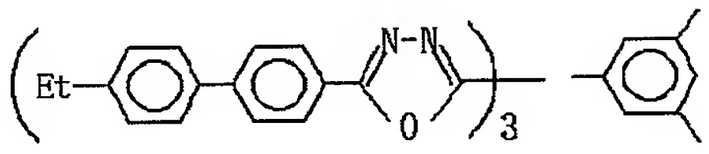
ETL19 

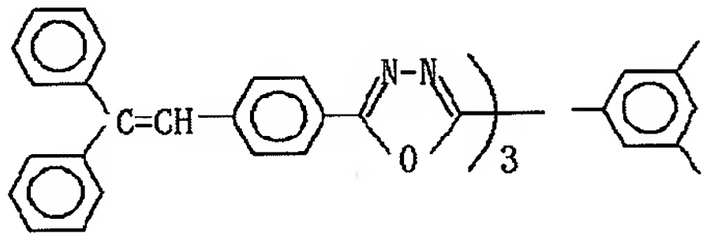
ETL20 

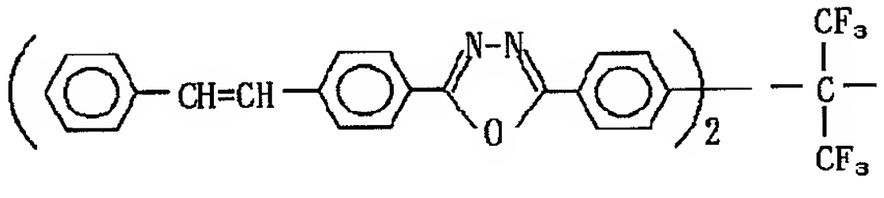
ETL21 

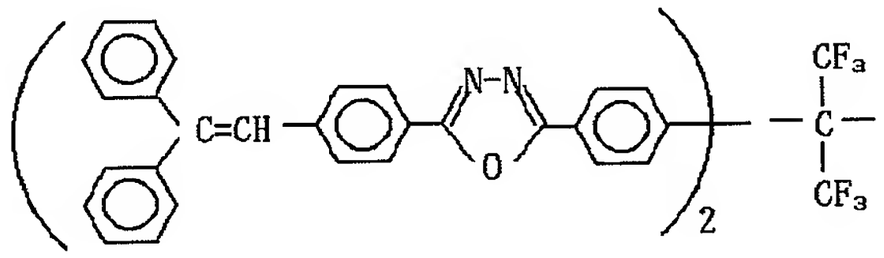
ETL22 

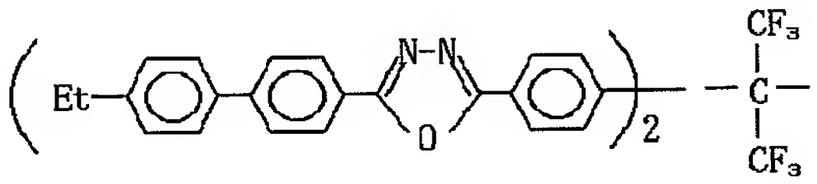
[0022]
[Table 3-(5)]

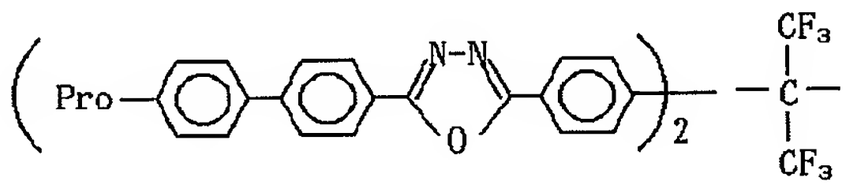
ETL23 

ETL24 

ETL25 

ETL26 

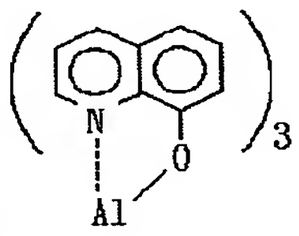
ETL27 

ETL28 

[0023]In order to use it for the electron injection transporting bed of the lamination EL element of this invention, especially a desirable organic substance is a metal chelate-ized oxy NOIDO compound including the chelate of 8-hydroxyquinoline. The thing of Table 4 can be mentioned below as an example.

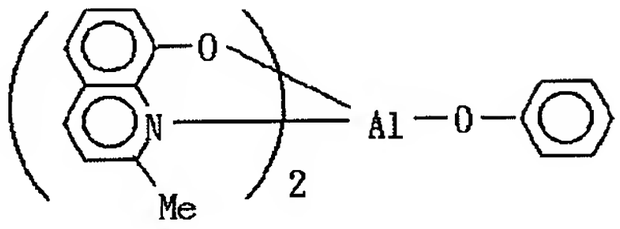
[0024]

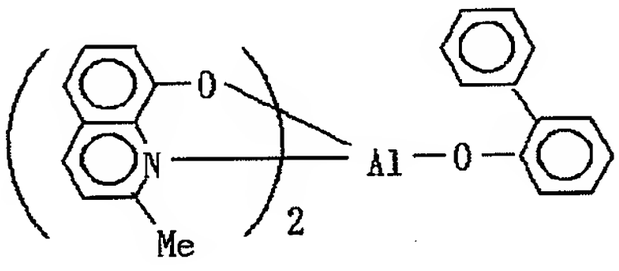
[Table 4-(1)]

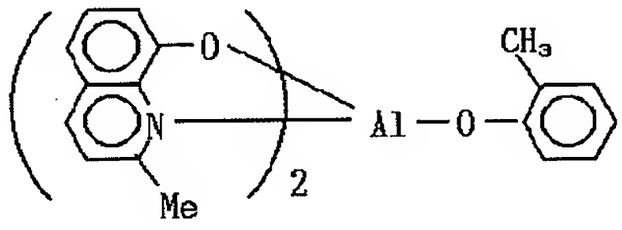
ETL29 Aluminumtrisoxine 

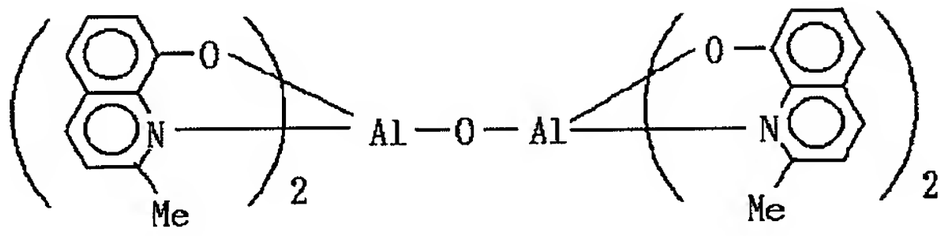
ETL30 magnesium screw oxine ETL31 bis(benzo-eight quinolinol)zinc ETL32 bis(2-methyl-8-quinolate)aluminum oxide ETL33 indiumtrisoxine ETL34 aluminum tris (5-methyloxine) ETL35 lithium oxine ETL36 galliumtrisoxine ETL37 Calcium screw (5-chlorooxine) ETL38 Poly (zinc (II)-bis(8-hydroxy-5-KINORI nonyl)methane) ETL39 Dilithium EPINDORI dione [0025]

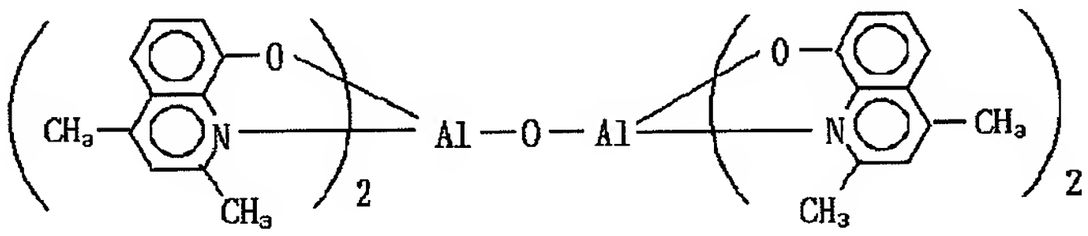
[Table 4-(2)]

ETL40 

ETL41 

ETL42 

ETL43 

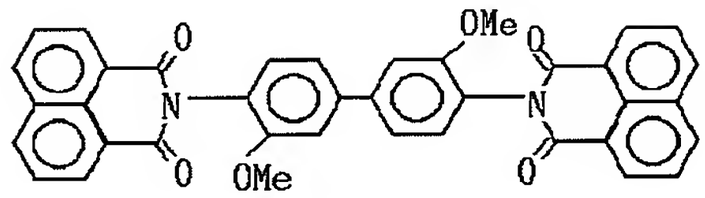
ETL44 

[0026]The screw type metal chelate-ized oxy NOIDO compound of USP5,151,629 and USP5,150,006 statement is also preferred as an electron injection transporting bed material. As other desirable electron injection transporting bed materials, A butadiene derivative like 1, 4 diphenylbutadiene, and tetraphenylbutadiene, A coumarin derivative, a screw styryl benzene derivative, a screw styryl anthracene derivative, A benzoxazole derivative, an oxadiazole derivative, an oxazole derivative, a thiadiazole derivative, a NAFUTARU imide derivative, a perylene diimidotetracarboxylic acid derivative, a quinacridone derivative, etc. can be mentioned. A concrete compound is mentioned to Table 5 below.

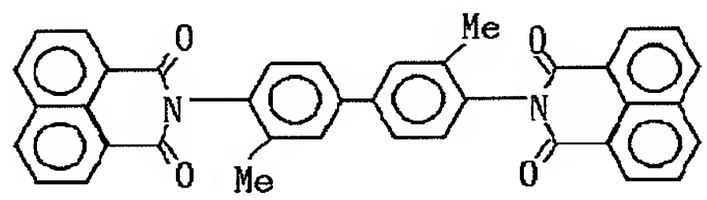
[0027]

[Table 5]

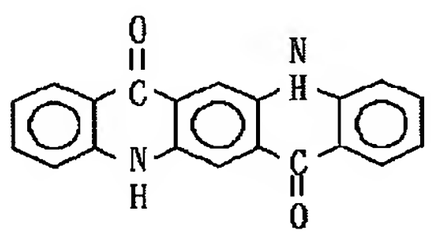
ETL45



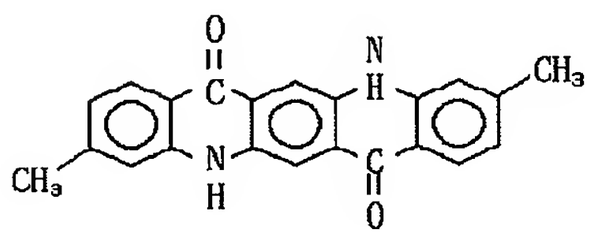
ETL46



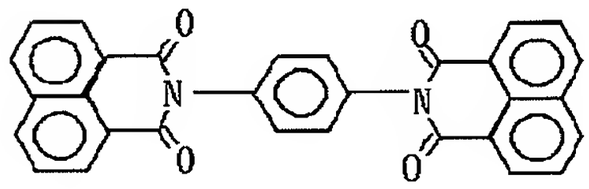
ETL47



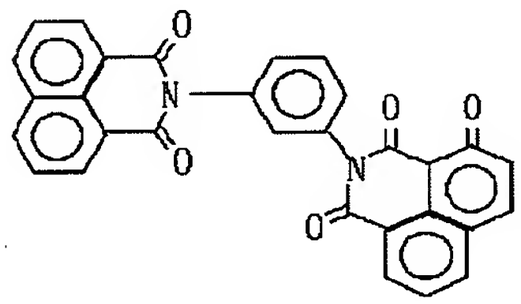
ETL48



ETL49



ETL50



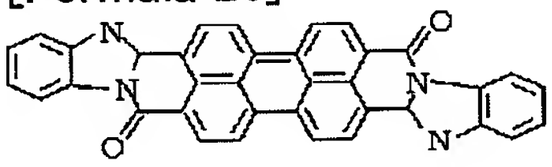
[0028]Although the example of a useful electron injection transported material has been shown above, when it constitutes an electron injection transporting bed from two or more layers, the laminating order which satisfies said formula (I) is preferred from a viewpoint of durability enhancement.

[0029]The organic thin film EL element in this invention the organic compound explained above by vacuum deposition method, the solution applying method, etc. The thickness thinner than 0.5 micrometer at the whole organic compound layer, and by thin-film-izing 1000A or less of each organic layer in thickness of 100A - 1000 A still more preferably preferably, an organic compound multilayer is formed and it is constituted by sandwiching with the anode and the negative pole. When a composition organic compound is remarkably rich in thin-film-forming ability, it is also possible to form a layer in thickness of 100A or less. The organic thin layer EL element of this invention may be a thing of the structure which between the organic layers which each adjoin, and between the electrode and the organic layer did not have a clear interface, but

formed the mixed mixing zone.
[0030]Hereafter, this invention is explained still in detail over a drawing. Drawing 1 provides the anode / hole pouring transporting bed / luminous layer / electron injection transporting bed / negative pole one by one. (Both the layers of **, a hole pouring transporting bed, and an electron injection transporting bed consist of a layer more than two-layer at least.)
Drawing 2 provides the anode / hole pouring transporting bed / luminous layer / negative pole one by one. (** and a hole pouring transporting bed consist of a layer more than two-layer at least.)
Drawing 3 provides the anode / luminous layer / electron injection transporting bed / negative pole one by one. (** and an electron injection transporting bed consist of a layer more than two-layer at least.)
[0031]Since there is an organic thin film EL element of this invention also when causing a short circuit and stopping functioning as an element by few pinholes although it makes voltage impress and emit light electrically to an EL element, it is desirable to use together the compound excellent in thin-film-forming nature for formation of an organic layer. A luminous layer can also be formed combining a compound and a polymer binder excellent in still such thin-film-forming nature. In this case, as a polymer binder which can be used, polystyrene, polyvinyl toluene, poly-N-vinylcarbazole, polymethylmethacrylate, polymethyl acrylate, polyester, polycarbonate, polyamide, etc. can mention.
[0032]As an anode material, nickel, gold, platinum, palladium and these alloys, or the tin oxide (SnO_2), Conductive polymers, such as big metal and those alloys of work functions, such as oxidation ****- indium (ITO) and copper iodide, a compound and also poly (3-methylthiophene), polypyrrole, and polyarylene vinylene, etc. can be used. On the other hand, as a cathode material, the small silver of a work function, tin, lead, magnesium, manganese, aluminum, or these alloys are used. In the luminous wavelength field of an element, the transparent enough thing of at least one side is desirable among the materials used as the anode and the negative pole. It is desirable to specifically have the light transmittance of not less than 80%.
[0033]In this invention, although it is desirable to form a transparent positive electrode on a transparent substrate, and to have composition like drawing 1 - drawing 3, depending on the case, it is very good in the reverse composition. Glass, a plastic film, etc. can be used as a transparent substrate. A protective layer is provided independently, or the whole element is put in a cell, and it may be made to enclose a silicone oil etc. in this invention for the protection to the improvement in the stability of the EL element produced by doing in this way, especially the moisture in the atmosphere.
[0034]
[Example]Based on an example, this invention is explained more concretely below.
[0035]The example 1(when electron injection transporting bed is formed from two-layer)ITO (indium stannic-acid ghost: sheet resistance 20ohm/**) board was cleaned ultrasonically with neutral detergent, acetone, and isopropyl alcohol one by one. And the ITO board was immersed in the boiled isopropyl alcohol for 5 minutes, and stoving was carried out to it. Hole pouring transporting bed material HTL1 [400A] was vapor-deposited by heating an alumina crucible under the vacuum of 10^{-6}torr. Next, luminous layer material EML1 [150A] was vapor-deposited. Next, 1st electron injection transporting bed ETL29 [200-A / 300A] was further vapor-deposited for 2nd electron injection transporting bed ETL1, and, finally 2000A of MgAg electrodes of the atomic ratio of 10:1 were vapor-deposited. Thus, the created EL element showed driver voltage 8.9V and light-emitting-luminance 620 cd/m^2 in the current density of 30 mA/cm^2 immediately after voltage impressing. Then, it maintained high-intensity [of 430 cd/m^2] also after 60-minute progress and 668cd/m^2 and 10-hour progress. The emission spectrum was the blue light centering on 475 nm. At this time, the work function of 3.0 eV and the negative pole of the electron affinity of 2.14 eV and the 1st electron injection transporting bed is 3.50 eV, and the electron affinity of the 2nd electron injection transporting bed satisfies the expression of relations according to claim 1.

Ipc(3.50eV)>Eae1(3.0eV)>Eae2(2.14eV) (III)
[0036]comparative example 1 (when an electron injection transporting bed is formed from a monolayer)
The EL element was created like Example 1 except having omitted 1st electron injection transporting bed ETL29. However, the thickness of the 2nd electron injection transporting bed was 500 A. In this case, the light emitting luminance of 520 cd/m^2 and the driver voltage 10V were observed under the constant current of 30 mA/cm^2 immediately after voltage impressing. However, after 1-hour progress, after 270cd/m^2 and 10-hour progress, when light-emitting-luminance 43 cd/m^2 and the 2nd electron injection transporting bed were omitted, endurance was remarkably inferior. Initial drive voltage also showed the value high 1.1v compared with Example 1. From this, when two or more electron injection transporting beds exist, it turns out that the improvement in endurance and the fall of driver voltage have an effect.
[0037]Example 2 (when a hole pouring transporting bed and an electron injection transporting bed are formed from two-layer, respectively)
The EL element was created like Example 1 except having inserted the copper phthalocyanine (HTL18) (CuPc) of 250 A of thickness in the anode and the interface of the 2nd hole pouring transporting bed (HTL1) as a 1st hole pouring transporting bed. However, the thickness of the 2nd hole pouring transporting bed was 200 A. In this case, it was an EL element which light-emitting-luminance 492cd/m^2 and the driver voltage 5.3V are observed under constant current immediately after voltage impressing, and high-intensity [of 260 cd/m^2] is observed after 10-hour progress, and is rich in endurance. From this, by forming a hole pouring transporting bed and an electron injection transporting bed from two or more layers shows that it becomes possible to reduce driver voltage remarkably. In this composition, the ionization potential of the ITO electrode which is the anode Ipa=4.53eV, The ionization potential of 1= 4.97 eV of Iph(s) and the 2nd hole pouring transporting bed is 2= 5.08 eV of Iph(s), and the ionization potential of the 1st hole pouring transporting bed satisfies the expression of relations according to claim 1.
Ipa(4.53eV)<Iph1(4.97eV)<Iph2(5.08eV) (III)
[0038]example 3 (when Quinacridone is used for the 1st electron injection transporting bed)
The EL element was created like Example 1 except having used triphenylamine derivative HTL2 for the hole pouring transporting bed, and having used quinacridone derivative ETL47 for the 1st electron injection transporting bed. In this case, immediately after voltage impressing, under the constant current of 30 mA/cm^2, the light emitting luminance of 250 cd/m^2 and the driver voltage 11V were observed, and the light emitting luminance of 100 cd/m^2 was observed after 10-hour progress. The electron affinity of a quinacridone compound is estimated at 2.60 eV, and satisfies the expression of relations according to claim 1.
Ipc(3.50eV)>Eae1(2.60eV)>Eae2(2.14eV) (V)
[0039]example 4 (when a NAFUTARU imide derivative is used for the 1st electron injection transporting bed)
The EL element was created like Example 1 except having used triphenylamine derivative HTL3 for the hole pouring transporting bed, and having used NAFUTARU imide derivative ETL45 for the 1st electron injection transporting bed. In this case, the light emitting luminance of 328 cd/m^2 and the driver voltage 9V were observed under the constant current of 30 mA/cm^2 immediately after voltage impressing. After 1-hour progress, the light emitting luminance of 528 cd/m^2 was observed, and the light emitting luminance more than 100 cd/m^2 was observed also after 10-hour progress. The electron affinity of this NAFUTARU imide compound is estimated at 2.70 eV, and satisfies the expression of relations according to claim 1.
Ipc(3.50eV)>Eae1(2.70eV)>Eae2(2.14eV) (VI)[0040]The EL element was created like comparative example 2 Example 1. However, the following perylene derivative (PV) was used for the 1st electron injection transporting bed. In this case, only weak EL luminescence was observed also in the impressed electromotive force 20V, but it was an element with very bad luminous efficiency. It was an element which luminosity reduces this element by half within 1 hour at when a

durability test is done under the constant current of 30 mA/cm^2, and is extremely inferior to endurance. In this case, the relation between the electron affinity of the 1st and 2nd electron injection transporting bed and the work function of the negative pole is Ipc(3.50 eV) >Eae1(4.30 eV)>Eae2 (2.14 eV) (V).
It is shown that the relation of the electronic character of the negative pole and the electron injection transporting bed which come out and exist, and do not satisfy the expression of relations according to claim 1, but satisfy the expression of relations of (I) is important for improvement in endurance.
[Formula 26]



PV

[0041]The EL element was created like five to example 8 Example 1. Lamination material and the durable characteristic are shown in following Table 7.
[0042]
[Table 7]

実施例	HTL	EML	ETL		0時間	1時間	10時間
			第2層	第1層	(cd/m^2)	(cd/m^2)	(cd/m^2)
5	HTL3	EML1	ETL1	ETL29	530	730	440
6	HTL1	EML2	ETL1	ETL29	650	570	440
7	HTL3	EML3	ETL1	ETL29	740	625	470
8	HTL3	EML4	ETL1	ETL29	400	480	390

These elements satisfy the expression of relations according to claim 1 between the negative pole and the 1st and 2nd electron injection transporting bed like Example 1.
[0043]Example 9 (pulse drive)
The EL element was created like Example 1. However, the thickness of the organic layer was set up as follows.
1st hole pouring transporting bed HTL1 400A luminous layer EML1 2nd electron injection transporting bed ETLof 150A6 1st electron injection transporting bed [of 200A] ETL29 Do in this way 300 A and the created EL element Peak current value/cm[of 30 mA] ^{2}, When driven by the square wave with a frequency of 100 Hz, initial luminance 85cd/m^2 and the driver voltage 6.2V were shown. Then, it was an EL element which is maintaining the light emitting luminance (driver voltage 8.6V) of 97 cd/m^2 after 201-hour progress, and is extremely rich in endurance.
[0044]The EL element was created like example 10 Example 2. However, ETL6 was used for the 2nd electron injection transporting bed. In this case, under the constant current of 30 mA/cm^2, light-emitting-luminance 60cd/m^2 and the driver voltage 6.2V were shown immediately after voltage impressing, initial luminance was maintained after 170-hour progress, and the result which is extremely rich in endurance was obtained. Also in this case, the electron affinity of 20 layers of ETL(s) is estimated at 2.5 eV, and satisfies the expression of relations according to claim 1.
Ipc(3.50eV)>Eae1(2.50eV)>Eae2(2.14eV) (VIII)[0045]example 11 (when an electron injection transporting bed is formed from three layers)

The ITO (indium stannic-acid ghost: sheet resistance 20ohm/**) board was cleaned ultrasonically with neutral detergent, acetone, and isopropyl alcohol one by one. And the ITO board was immersed in the boiled isopropyl alcohol for 5 minutes, and stoving was carried out to it. Hole pouring transporting bed material HTL1 [400A] was vapor-deposited by heating an alumina crucible under the vacuum of 10^{-6}torr. Next, luminous layer material EML1 [150A] was vapor-deposited. Next, 1st electron injection transporting bed ETL29 [150-A / 250A] was further vapor-deposited [3rd electron injection transporting bed ETL1] for 150 A and 2nd electron injection transporting bed ETL6, and, finally 2000A of MgAg electrodes of the atomic ratio of 10:1 were vapor-deposited. Thus, the created EL element showed driver voltage 7.6V and light-emitting-luminance 510 cd/m^2 in the current density of 30 mA/cm^2 immediately after voltage impressing. Then, it maintained high-intensity [of 420cd//m / ^{2}] also after after [60 minute progress] 610cd/m^2, and 10-hour progress. At this time, the electron affinity of the 3rd electron injection transporting bed is 3.50 eV, and, as for the work function of 3.0 eV and the negative pole, the electron affinity of 2.50 eV and the 1st electron injection transporting bed satisfies [the electron affinity of 2.14 eV and the 2nd electron injection transporting bed] the expression of relations according to claim 1. Ipc(3.50eV)>Eae1(3.0eV)>Eae2(2.50eV)>Eae3 (2.14eV) (IX) [0046]The EL element was created like Example 11 except having used the copper phthalocyanine (CuPc) (HTL18) as an example 12 1st hole pouring transporting bed, and having used HTL1 [200A] as 200 A and a 2nd hole pouring transporting bed. Thus, the created EL element showed driver voltage 6.6V and light-emitting-luminance 490 cd/m^2 in the current density of 30 mA/cm^2 immediately after voltage impressing. Then, it maintained high-intensity [more than 400 cd/m^2] also after 10-hour progress. In this case, compared with Example 11, the fall of driver voltage was able to be aimed at by inserting a copper phthalocyanine. [0047]After washing a substrate like example 13 Example 11, a copper phthalocyanine (CuPc) (HTL18) as a 1st hole pouring transporting bed 200 A, As a 2nd hole pouring transporting bed, 150 A and luminous layer EML1 were vapor-deposited for 150 A and 3rd hole pouring transporting bed HTL2, 200 A and 1st electron injection transporting bed ETL29 [300A] were vapor-deposited [HTL1] for 150 A and 2nd electron injection transporting bed ETL1, and, finally the MgAg alloy electrode was formed. Thus, the created EL element showed driver voltage 6.4V and light-emitting-luminance 530 cd/m^2 in the current density of 30 mA/cm^2 immediately after voltage impressing. Then, it maintained high-intensity [of 460cd//m / ^{2}] also after after [60 minute progress] 560cd/m^2, and 10-hour progress. In this element, the work function of 3.0 eV and the negative pole of the electron affinity of 2.14 eV and the 1st electron injection transporting bed is 3.5 eV, and the electron affinity of the 2nd electron injection transporting bed satisfies the expression of relations according to claim 1.
Ipc(3.50eV)>Eae1(3.0eV)>Eae2(2.14eV) (X)
The ionization potential of 5.08 eV and the 3rd hole pouring transporting bed of the ionization potential of 4.97 eV and the 2nd hole pouring transporting bed is 5.32 eV, and the ionization potential of the 1st hole pouring transporting bed satisfies the expression of relations according to claim 2.
Ipa(4.53eV)<Iph1(4.97eV)<Iph2(5.08eV)<Iph3(5.32eV) (XI)[0048]The EL element was created like comparative example 3 Example 13. However, ETL1 (200A) was used for the 1st electron injection transporting bed, ETL29 (300A) was used for the 2nd electron injection transporting bed, and laminating order was changed. Thus, in the current density of 30 mA/cm^2, although the created EL element showed driver voltage 8.4V and light-emitting-luminance 517 cd/m^2, it was immediately after voltage impressing the result of obtaining only the light emitting luminance below 100 cd/m^2, but after 10-hour progress being inferior to endurance. Although it was the blue EL luminescence centering on 475 nm in Example 13, when laminating order was made reverse, the EL luminescence from the 2nd electron injection transporting bed was also observed, and it was the green emission centering on 515 nm. In this element, the work function of 3.0 eV and the negative pole of the electron affinity of 2.14 eV and the 2nd electron injection

transporting bed is 3.5 eV, and the electron affinity of the 1st electron injection transporting bed does not satisfy the expression of relations according to claim 1.
Ipc(3.50eV)>Eae1(2.14eV)>Eae2(3.0eV) (XII)[0049]After processing a substrate like example 14 Example 11, 200A of copper phthalocyanines (CuPc) (HTL18) were vapor-deposited by heating an alumina crucible under the vacuum of 10^{-6}torr as a 1st hole pouring transporting bed. HTL1 was vapor-deposited as a 2nd hole pouring transporting bed, and HTL2 [150A] was vapor-deposited as 150 A and a 3rd hole pouring transporting bed. Next, luminous layer material EML1 [150A] was vapor-deposited. 1st electron injection transporting bed ETL29 [150-A / 250A] was further vapor-deposited [3rd electron injection transporting bed ETL1] for 150 A and 2nd electron injection transporting bed ETL6, and, finally 2000A of MgAg electrodes of the atomic ratio of 10:1 were vapor-deposited. Thus, the created EL element showed driver voltage 7.1V and light-emitting-luminance 523 cd/m^2 in the current density of 30 mA/cm^2 immediately after voltage impressing. Then, it maintained high-intensity [of 480 cd/m^2] also after 10-hour progress. In this case, the work function of 3.0 eV and the negative pole of the electron affinity of 2.14 eV and the 2nd electron injection transporting bed is 3.50 eV, and the electron affinity of the 3rd electron injection transporting bed satisfies the expression of relations according to claim 1.
Ipc(3.50 eV) >Eae1(3.0 eV)>Eae2(2.50 eV)>Eae3 (2.14 eV) (XIII).The ionization potential of 5.08 eV and the 3rd hole pouring transporting bed of the ionization potential of 4.97 eV and the 2nd hole pouring transporting bed is 5.32 eV, and the ionization potential of the 1st hole pouring transporting bed satisfies the expression of relations according to claim 2.
Ipa(4.53eV)<Iph1(4.97)eV)<Iph2(5.08eV)<Iph3(5.32eV) (XIV)[0050]The EL element was created like 15 to example 22 Example 1. Lamination material and the durable characteristic are shown in following Table 8. These elements satisfy the expression of relations according to claim 1 between the negative pole and the 1st and 2nd electron injection transporting bed.
[0051]
[Table 8]

実施例	HTL	EML	ETL		0時間	1時間	10時間
			第2層	第1層	(cd/m²)	(cd/m²)	(cd/m²)
15	HTL1	EML1	ETL2	ETL29	670	630	360
16	HTL1	EML1	ETL11	ETL29	494	350	150
17	HTL1	EML1	ETL13	ETL29	680	620	420
18	HTL1	EML1	ETL12	ETL29	790	680	310
19	HTL1	EML1	ETL7	ETL29	78	113	145
20	HTL1	EML1	ETL5	ETL29	115	201	134
21	HTL1	EML2	ETL5	ETL29	460	430	280
22	HTL1	EML1	ETL9	ETL29	60	80	89

[0052]
[Effect of the Invention]The organic thin film EL element of this invention can transform

electrical energy into light energy directly by the recombination of the electrification carrier (an electron and a hole) poured into the luminous layer by the applied electric field, Unlike EL of the conventional incandescent lamp, a fluorescent lamp, or an inorganic compound, etc., with the light emitting diode of an inorganic compound, realization of the blue light which was difficult for realization is enabled, By making into two or more layers both a luminous layer, an inter-electrode hole pouring transporting bed, an electron injection transporting bed, or any to be in an organic thin film EL element, it becomes possible to aim at improvement in endurance.

[Translation done.]

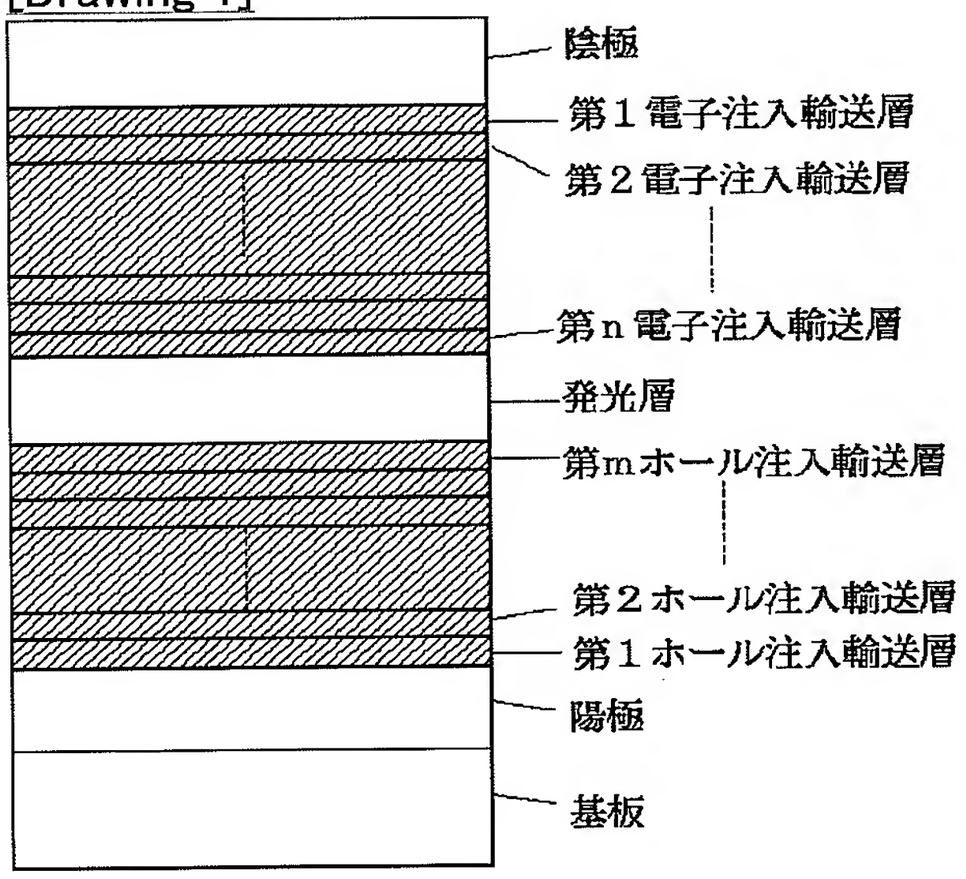
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a type section figure of the organic thin film EL element concerning this invention.
[Drawing 2]It is a type section figure of other organic thin film EL elements concerning this invention.
[Drawing 3]Furthermore it is involved in this invention, it is a type section figure of other organic thin film EL elements.
[Description of Notations]
m ... Integer which shows two or more turn from the anode side of the hole pouring transporting bed of a layer.
n ... Integer which shows two or more turn from the negative pole side of the electron injection transporting bed of a layer.

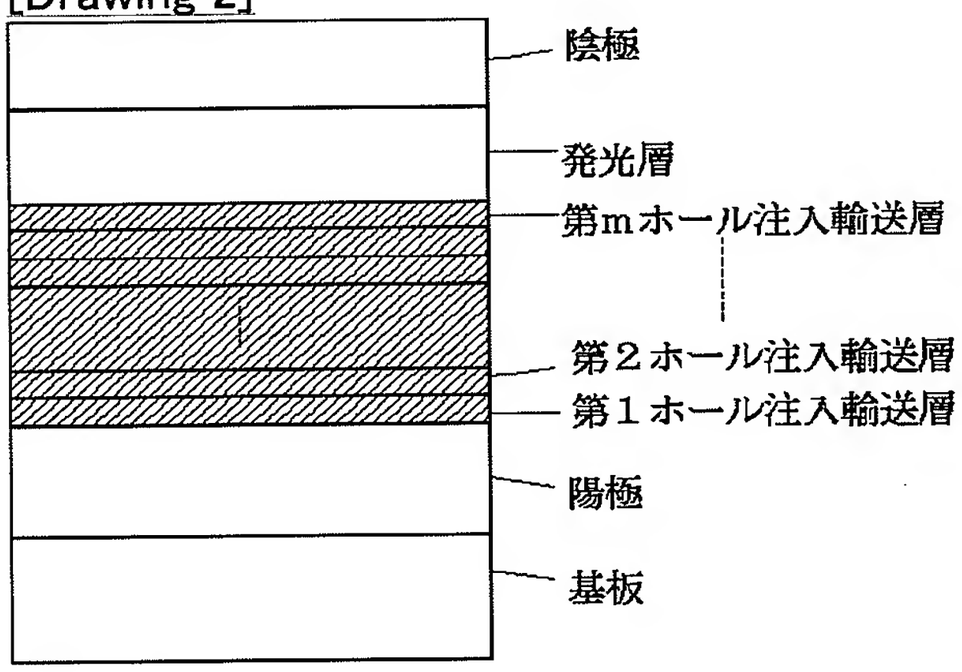
[Translation done.]

DRAWINGS

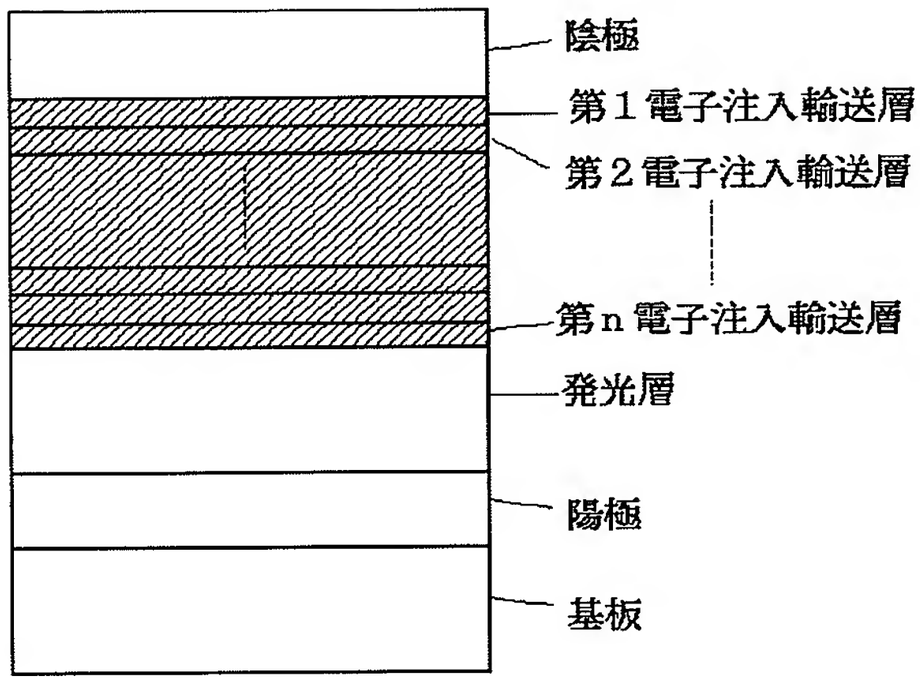
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]